

Technical Note N-1402

DURABILITY OF PLASTICS IN ANAEROBIC MARINE SEDIMENTS

By

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October 1975



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T4
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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER TN-1402	2. GOVT ACCESSION NO. DN544144	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) DURABILITY OF PLASTICS IN ANAEROBIC MARINE SEDIMENTS		5. TYPE OF REPORT & PERIOD COVERED Final; 1 Jul 1972-31 Jun 1975
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) J. S. Muraoka and H. P. Vind		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS CIVIL ENGINEERING LABORATORY Naval Construction Battalion Center Port Hueneme, California 93043		10. PROGRAM ELEMENT PROJECT, TASK AREA & WORK UNIT NUMBERS 62755N; YF54.543.007.01.001
11. CONTROLLING OFFICE NAME AND ADDRESS Naval Facilities Engineering Command Alexandria, Virginia 22332		12. REPORT DATE October 1975
		13. NUMBER OF PAGES 14
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Durability, plastics, deterioration of materials, marine environment, hydrogen sulfide, harbor mud, electric cable, rubber, rope.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Specimens of a wide variety of plastic sheets, ropes, and electrical cable insulations were partially buried in anaerobic harbor sediments to determine the effect of hydrogen sulfide on polymeric materials. For comparison, specimens of the same materials were exposed in aerobic surface waters. After 2-1/2 years, the specimens were all recovered. Very little change was noted in the appearance, strength, or hardness of any of the specimens of synthetic polymeric materials. In contrast, nothing remained of samples		

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DURABILITY OF PLASTICS IN ANAEROBIC MARINE
SEDIMENTS (Final), by J. S. Muraoka and H. P. Vind
TN-1402 14 p. illus October 1975 Unclassified

1. Material deterioration 2. Marine environment I. YF54.543.007.01.001

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INTRODUCTION

Anaerobic environments are usually found in the oceans wherever circulation of oxygenated seawater is restricted or where decaying organic matter is discharged. Anaerobic ocean areas frequently occur in harbors and bays and adjacent sewage outfalls.

In an anaerobic marine environment, hydrogen sulfide is always liberated. As long as free oxygen is present, marine bacteria utilize it to oxidize organic matter. In the absence of free oxygen, the bacteria oxidize their food by reducing sulfate ions in the seawater, and hydrogen sulfide is evolved in the process.

Hydrogen sulfide greatly accelerates the corrosion of iron and steel [1]. It is reported [2, 3] that iron and steel pipes, pumps, storage tanks, piling, mooring chains, ship hulls, and painted metal surfaces corrode rapidly in an anaerobic environment where copious quantities of hydrogen sulfide are present.

Tests were undertaken at the Civil Engineering Laboratory (CEL) to ascertain if structural plastics and other polymeric materials also undergo rapid deterioration in an anaerobic environment. This report describes the CEL tests in which specimens of a wide variety of plastic sheeting, electrical cable insulation, and synthetic fiber ropes were exposed to an anaerobic marine environment for 2-1/2 years. For comparison, natural fiber ropes, wood, and rubber were also subjected to the same environment. For further comparison, all of the materials were also placed in aerobic, near-surface waters.

MATERIALS AND METHODS

Test Specimens

Several 6- by 12-inch panels were cut from sheets of the plastic materials listed in Table 1. The sheets of polytetrafluoroethylene and polyurethane were each 1/16 inch thick; all of the other sheets were 1/8 inch thick. Rope specimens approximately 2 feet in length with eyesplices formed at each end were prepared from each of the materials listed in Table 2. The diameter of the cotton ropes was 1/2 inch, and the diameter of all the others was 1/4 inch. Ten-inch lengths of insulated electrical cable covered with the materials designated in Figure 1 were mounted on plastic panels having dimensions of 1/8 by 6 by 12 inches. Panels of Douglas fir measuring 1/4 by 6 by 12 inches were also prepared for the tests.

Table 1. Properties of Plastic Sheeting Exposed in Ocean 2-1/2 Years

Plastic	Durometer Hardness Reading			Tensile Strength (psi)			Moisture Absorption (% of dry weight)	
	Control	Anaerobic	Aerobic	Control	Anaerobic	Aerobic	Anaerobic	Aerobic
Methyl methacrylate	89	88	89	1,016 ±89	887 ±68	1,016 ±55	0.9	0.9
Nylon	72	74	73	593 ±18	580 ±5	551 ±11	5.6	5.7
Phenol-formaldehyde ^a	92	91	91	1,616 ±17	1,372 ±106	1,318 ±201	2.6	1.8
Polycarbonate	83	83	83	865 ±66	933 ±9	913 ±6	-0.4	0.1
Polyethylene	47	47	48	1,452 ±70	1,363 ±20	1,394 ±20	-0.1	0.1
Polypropylene	73	76	75	489 ±7	485 ±12	485 ±2	0.2	0.1
Polystyrene	82	82	82	320 ±3	305 ±3	324 ±13	0.2	0.3
Polytetrafluoroethylene	57	56	57	324 ±0	372 ±6	383 ±17	0.2	0.3
Polyurethane	95 ^a	96 ^d	95 ^d	431 ±49	441 ±59	530 ±25	1.3	1.2
Poly(vinyl chloride)	84	84	83	800 ±25	767 ±5	822 ±1	0.1	0.2

^a Type A durometer was used; a type D durometer was employed for all other tests.

Table 2. Tensile Strength of Ropes

Rope Material	Force to Break		
	Unexposed	Anaerobic Exposure	Aerobic Exposure
Cotton ^a	1,825	0	0
Dacron	1,400 1,550	1,350 1,250	1,340 1,350
Manila Hemp ^a	725 635	0 0	0 0
Nylon	1,350 1,375	1,310 1,300	1,350 1,330
Polypropylene	1,150 1,150	925 950	1,025 1,050

^a The exposed cotton and manila hemp ropes had disintegrated before the tests were performed.

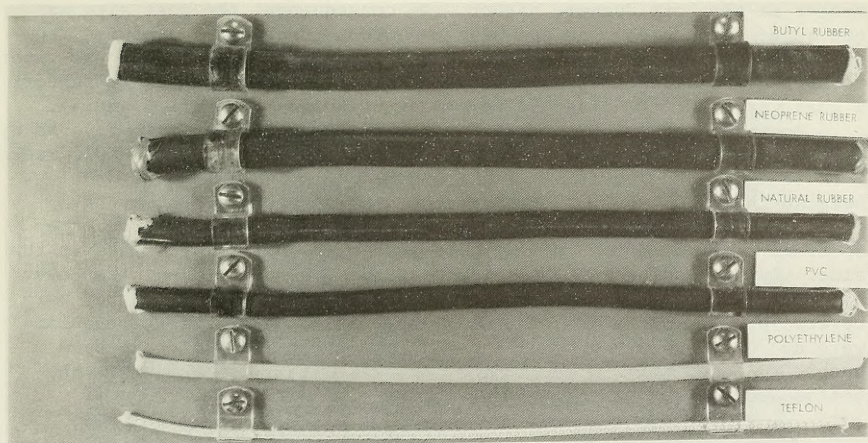


Figure 1. Specimens of insulated electric cable ready for exposure in the ocean.

Exposure Racks

All of the test specimens were mounted on racks as shown in Figure 2. Each of the panels was held in place by four molded, grooved, polyethylene insulators and were separated from each other by 1 inch. The center dividers and end plates were titanium alloy 75-A. The tie rods through the insulators were nickel-copper alloy 400 fastened with nuts and washers of the same composition. Poly (vinyl chloride) (PVC) washers were used between the metal washers and the end plates. The rope specimens were wrapped around the racks in such a way that the center sections of the ropes would be embedded in the mud and the eye-splices would be held out of the mud at the tops of the titanium racks. Four such racks were prepared in replicate.

Anaerobic Test Site

The Port Hueneme harbor anaerobic test site was selected during the preliminary stages of this investigation. The harbor bottom was known to be stagnant at the site which was near the mouth of a small drainage ditch and underneath the ship-berthing area. Debris from the drainage ditch and wastes from the ships contributed to the development of an anaerobic harbor bottom.

Stringent regulations on the discharge of wastes from shore and from ships have resulted in a decrease in the quantities of organic matter in the Port Hueneme harbor. In consequence, the test site was not quite as anaerobic as had been expected. Grab samples of mud from the test site area still had the odor of hydrogen sulfide, but the water a short distance from the bottom contained sufficient oxygen to support a scant growth of fouling and burrowing organisms (Figures 3 and 4).

Ocean or harbor bottoms in anaerobic areas are typically covered by thick layers of soft mud. It was anticipated that when the sample racks were lowered, they would sink into the mud layer, but they did not because this mud layer was not as thick as expected. As a result, divers had to shovel harbor bottom sediments and partially cover the specimen racks with the sand, gravel, and other bottom sediments at the site. By the end of the 2-1/2-year exposure period, most of the cover had apparently been removed from the specimen racks, because they were covered by a scant growth of fouling organisms. The fouling organisms were not of the mud-burrowing type; they would ordinarily have been unable to reach the sample rack had it been completely buried in the bottom sediments.

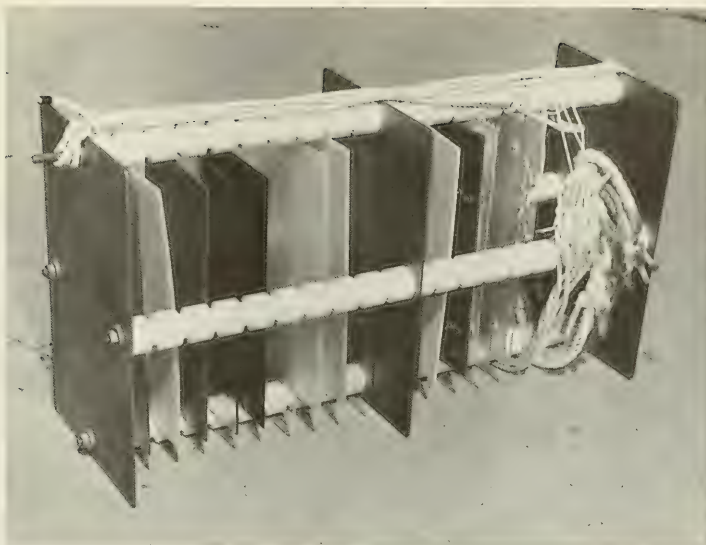


Figure 2. Rack with specimens mounted ready for exposure in the ocean.

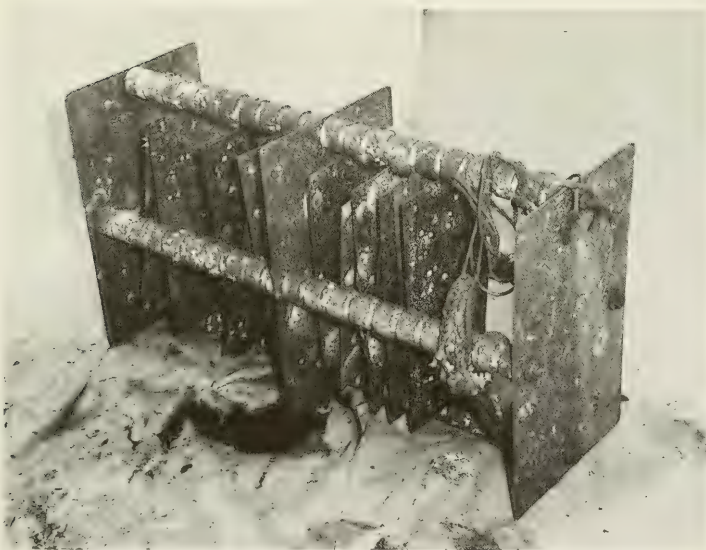


Figure 3. Rack of specimens exposed in anaerobic mud for 2-1/2 years.

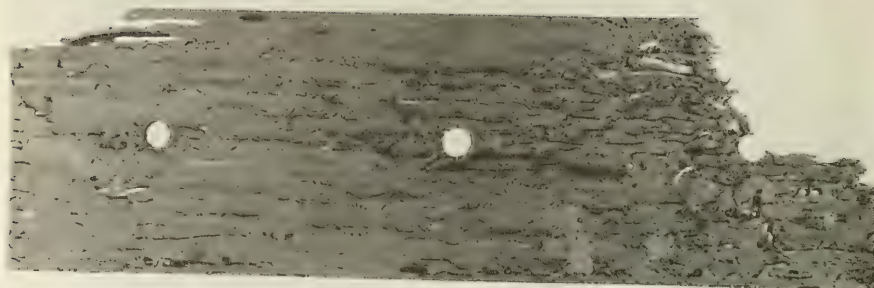


Figure 4. Specimen of wood exposed for 1 year at mud line.

Harbor Exposure Tests

Two of the test racks with specimens all mounted as in Figure 2 were placed in the black and anaerobic bottom sediments of the Port Hueneme harbor. One of the racks was recovered after 1 year, and the specimens were examined to obtain data for a preliminary report on the durability of plastics in anaerobic sediments [4]. The other rack was exposed partially buried in the anaerobic bottom sediments for 2-1/2 years (Figure 3).

The third of the replicate test racks on which the specimens of polymeric materials were mounted was suspended for 2-1/2 years from the materials-testing dock at Port Hueneme. This rack was exposed at a depth of 3 feet below the low tide line. (Figure 5 shows the fouling organisms attached to the rack after this period.)

The fourth and final replicate test rack was stored in the laboratory for a period of 2-1/2 years, and the specimens were maintained as controls.

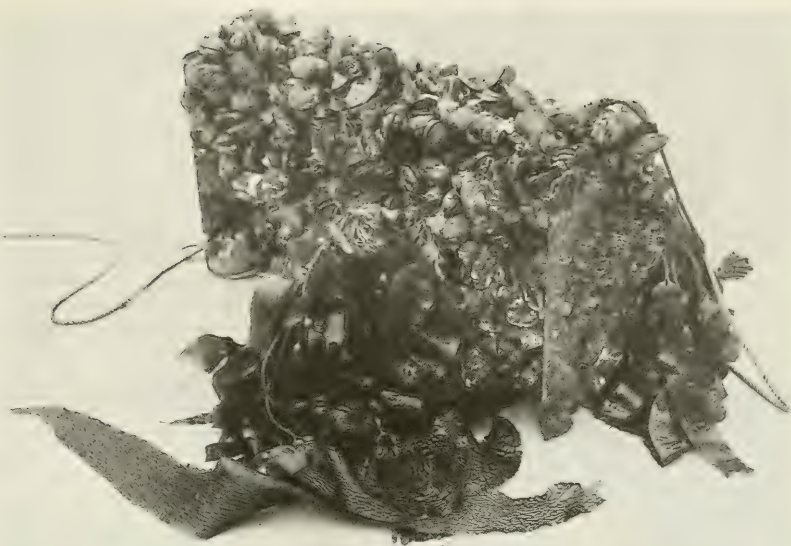


Figure 5. Rack of specimens engulfed in fouling after 2-1/2-year exposure near ocean surface.

Measurements of Water Absorption

The panels of plastic sheeting were removed from the test racks and cleaned immediately after they were removed from the harbor. The large fouling organisms were removed with a large putty knife, and the panels were scrubbed in seawater with a steel wire scrubbing pad. They were then rinsed in distilled water, wiped with paper towels, and air dried for 10 minutes to remove surface moisture. The panels were weighed to determine the weight of the panels plus the moisture they had absorbed. The panels were stored for 2 weeks in a 37°C drying room to remove the absorbed water from the panels; they were then weighed daily until their weights were constant. The loss in weight from the initial to the final weighing were measures of the moisture absorption of the panels (Table 1).

Hardness Tests

Measurements of the hardness of the dried panels of rigid plastic sheeting were conducted by the ASTM method described in Reference 5. A type A durometer was employed for testing the sheets of polyurethane and a type D durometer for all of the others. The average of five readings was used for each measurement (Table 1).

Tensile-Strength Tests

The tensile strengths of the dried panels of plastic sheeting were determined by the ASTM method described in Reference 6. In this method, specimens 1 by 6 inches are cut from the panels. As shown in Figure 6, the tensile-strength specimens are made narrower at the center than at the ends and resemble a double bladed paddle. The specimens are gripped at the ends by the jaws of the tensile-strength tester, and the loads required to break the specimens are determined. The load values are divided by the cross sectional areas of the panels at the site of the break, and they are reported as pounds per square inch to break (Table 1). The strengths of the rope specimens were also tested on the tensile testing machine. The specimens were gripped by the eye-splices and loaded to failure. The data are reported in terms of pounds of force required to break the rope specimens (Table 2).

EXPERIMENTAL FINDINGS AND DISCUSSION

The fouling growth which accumulated in 2-1/2 years on the specimens exposed partially buried in anaerobic mud was very scant (Figure 3). In contrast, the fouling which accumulated on the specimens exposed near the surface of the ocean was extremely abundant (Figure 5).

After a 1-year exposure (described in Reference 4) the cotton ropes (Figure 7) and Manila hemp ropes (Figure 8) had deteriorated so severely that the fibers could easily be torn apart by hand. The 1/4- by 6- by 12-inch Douglas fir panel that was exposed immediately above the bottom sediment was riddled by *Bankia* and *Teredo* (molluscan borers) and also by *Limnoria* and *Chelura* (crustacean borers) as shown in Figure 4. After 2-1/2 years in the harbor, nothing remained of either the cotton or hemp ropes or of the Douglas fir panels.

Panels

There were no significant differences in the amounts of water absorbed by plastic panels exposed for 2-1/2 years in the anaerobic bottom sediments and in the aerobic near-surface waters. Moisture absorption by the specimens of nylon sheet was approximately 6% of their dry weight. The panels of phenol-formaldehyde sheeting picked up approximately 2% of their dry weight in moisture; and the polyurethane and methyl methacrylate sheeting, approximately 1%. The other plastics absorbed negligible quantities of moisture.

The polymer that absorbs the most water would seem to have the greatest opportunity to react with water or with substances dissolved in it. However, inertness of the polymer molecules would also have to be considered. In seawater, nylon might deteriorate more rapidly than the other plastics tested; phenol-formaldehyde resin next, and so on because they absorb more water.

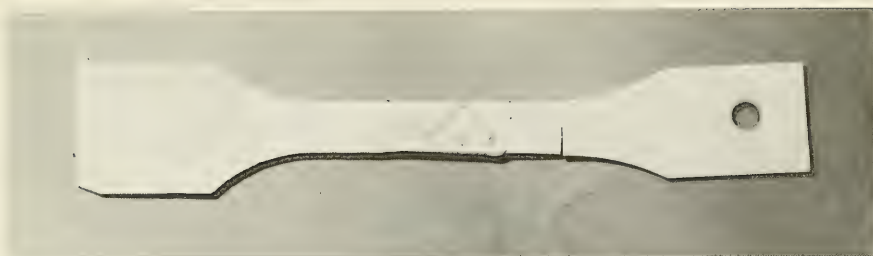


Figure 6. Plastic specimen for tensile-strength test.



Figure 7. Specimens of cotton rope exposed in harbor mud 1 year.

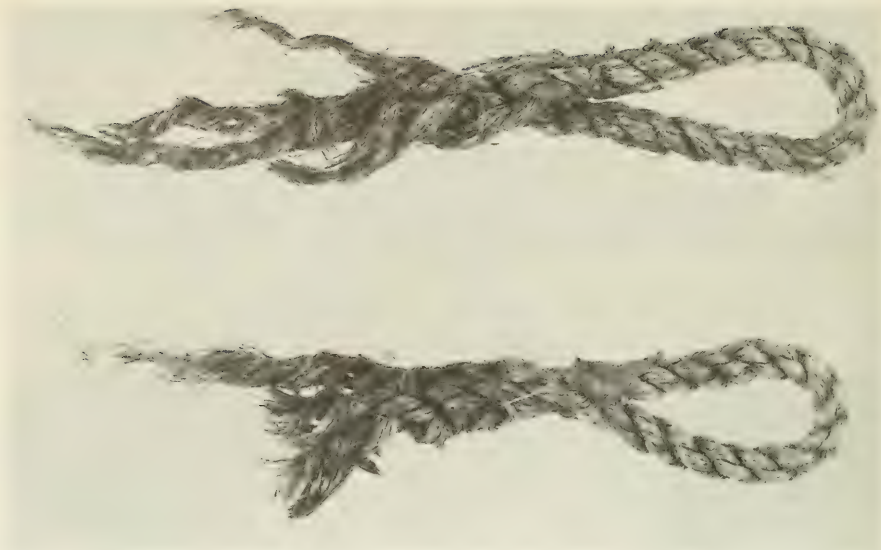


Figure 8. Specimens of Manila hemp ropes exposed in harbor mud 1 year.

There were no significant differences in the hardness or tensile strength of specimens of plastic sheeting exposed for 2-1/2 years in the anaerobic bottom sediments, in the aerobic near-surface waters, or in the laboratory (Table 1).

Ropes

Although synthetic fiber ropes changed somewhat in color after an exposure of 2-1/2 years in the ocean, they were weakened only slightly, if at all. Table 2 indicates that the ropes exposed in the harbor mud may have been a little weaker than unexposed ropes or those that were exposed in aerobic near-surface waters. In view of the small numbers of specimens tested, however, the differences were too small to be significant.

Electrical Cables

No physical tests were performed on the sections of insulated electrical cable (Figures 9 and 10). Microscopic examination of the outer covers of the cables disclosed that the natural rubber covers underwent surface deterioration. The small brackets holding the cable sections to the panels protected the surface of the underlying rubber.



Figure 9. Specimens of insulated electrical cable after 2-1/2-year exposure in the harbor mud.

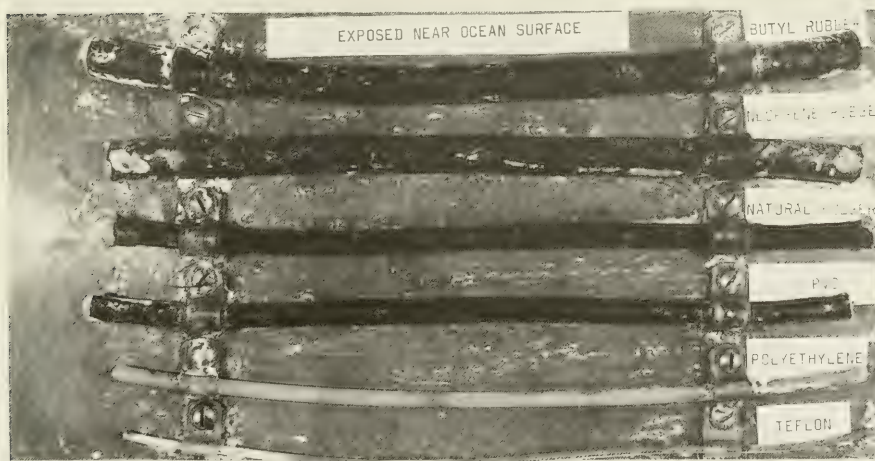


Figure 10. Specimens of insulated electrical cable after 2-1/2-year exposure near the surface of the ocean.

Sufficient rubber was eroded from the unprotected area of the cover to cause the diameter to visibly neck down at the edges of the brackets. This phenomenon was not observed on the synthetic-rubber-covered or plastic-covered cables. Neither of the latter appeared to be affected by 2-1/2 years of exposure either in the anaerobic bottom sediments or in the aerobic near-surface waters.

CONCLUSIONS

Many synthetic polymeric materials can withstand prolonged exposures in the ocean, either in the anaerobic bottom sediments or in the aerobic near-surface waters. After 2-1/2 years in the ocean they underwent essentially no measurable change in tensile strength or hardness.

The durability of plastic polymers might be related to their level of moisture absorption. Because of their extreme water repellency, it is predicted that the following six polymers would be the most durable in an ocean environment: polycarbonate, polyethylene, polypropylene, polystyrene, polytetrafluoroethylene, and poly (vinyl chloride). Next to the most durable in order of decreasing durability would be methyl methacrylate, polyurethane, phenol-formaldehyde, and nylon. Hydrophilic materials, such as cotton hemp and wood, are not durable in the ocean. The wettability and durability characteristics of natural rubber fall between the two extremes.

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